

EXPERIMENTAL INVESTIGATION OF SPACE RADIATION PROCESSING IN LUNAR SOIL ILMENITE: COMBINING PERSPECTIVES FROM SURFACE SCIENCE AND TRANSMISSION ELECTRON MICROSCOPY. R. Christoffersen^{1,2}, L. P. Keller¹, C. Dukes³, Z. Rahman^{1,2} and R. Baragiola³, ¹ARES, Mail Code KR, NASA Johnson Space Center, Houston, TX, 77058, roy.christoffersen-1@nasa.gov, ²Jacobs Technology, ESCG, Mail Code JE23, Houston, TX, 77058, ³Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, VA 22904.

Introduction. Energetic ions mostly from the solar wind play a major role in lunar space weathering because they contribute structural and chemical changes to the space-exposed surfaces of lunar regolith grains. In mature mare soils, ilmenite (FeTiO_3) grains in the finest size fraction have been shown in transmission electron microscope (TEM) studies to exhibit key differences in their response to space radiation processing relative to silicates [1,2,3]. In ilmenite, solar ion radiation alters host grain outer margins to produce 10-100 nm thick layers that are microstructurally complex, but dominantly crystalline compared to the amorphous radiation-processed rims on silicates [1,2,3]. Spatially well-resolved analytical TEM measurements also show nm-scale compositional and chemical state changes in these layers [1,3]. These include shifts in Fe/Ti ratio from strong surface Fe-enrichment ($\text{Fe/Ti} \gg 1$), to Fe depletion ($\text{Fe/Ti} < 1$) at 40-50 nm below the grain surface [1,3]. These compositional changes are not observed in the radiation-processed rims on silicates [4].

Several mechanism(s) to explain the overall relations in the ilmenite grain rims by radiation processing and/or additional space weathering processes were proposed by [1], and remain under current consideration [3]. A key issue has concerned the ability of ion radiation processing alone to produce some of the deeper-penetrating compositional changes. In order to provide some experimental constraints on these questions, we have performed a combined X-ray photoelectron spectroscopy (XPS) and field-emission scanning transmission electron (FE-STEM) study of experimentally ion-irradiated ilmenite. A key feature of this work is the combination of analytical techniques sensitive to changes in the irradiated samples at depth scales going from the immediate surface (~5 nm; XPS), to deeper in the grain interior (5-100 nm; FE-STEM).

XPS Methods and Results: A synthetic FeTiO_3 powder was used in order to meet sample volume requirements for XPS and match the Fe/Ti stoichiometry and Fe oxidation state of lunar ilmenites. Baseline high-resolution scans of the Fe and Ti 2p peaks in this material show Fe and Ti are primarily in the +3 and +4 oxidation states respectively, likely the result of atmospheric reactions operating on the 1-5 nm depth scales probed by XPS. Following acquisition of the baseline XPS scans the sample was immediately ion-

irradiated *in-situ* with 4 keV He^+ ions to a first dose of $1 \times 10^{17} \text{ He}^+/\text{cm}^2$ and a final dose of $3 \times 10^{17} \text{ He}^+/\text{cm}^2$, with XPS data acquired after each irradiation. Based on shifts in binding energy of the Fe and Ti 2p peaks, the post-irradiation XPS spectra at each dose step show conversion of surface Fe from +3 to a mixture of +2 and 0 (metallic) state at the first dose step, and then ultimately to a final, nearly complete, metallic state (Fig. 1). In addition, Ti progresses with ion dose from +4 to a mixture of more reduced states, likely +3 and +2 (Fig. 2). These chemical state changes are accompanied by a progressive factor of 2 to 3 decrease in surface O/Fe and O/Ti atomic ratios, showing dramatic surface O loss by preferential sputtering. A less dramatic 15-30% decrease in Fe/Ti ratio is also observed as irradiation progresses, consistent with some preferential sputtering of Fe relative to Ti.

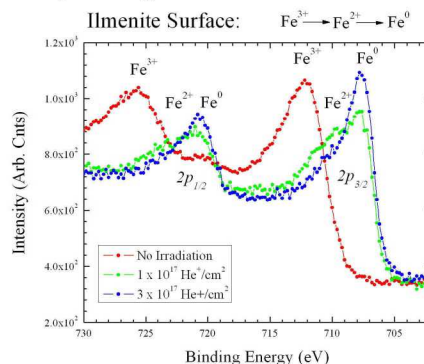


Figure 1. High-resolution XPS spectrum of Fe 2p region: Photoelectron peak positions for ilmenite sample before and after irradiation with 4 keV He^+ ions.

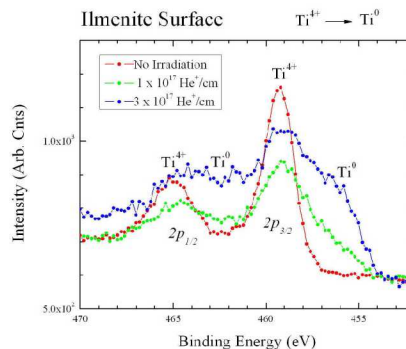


Figure 2. High-resolution XPS spectrum of Ti 2p region: Photoelectron peak positions for ilmenite sample before and after irradiation with 4 keV He^+ ions.

FE-STEM Methods and Results: For TEM study, a focused ion beam (FIB) section was extracted from the top surface of a 10 μm -diameter irradiated ilmenite grain from the uppermost layer of the XPS sample. Surface damage artifacts from the FIB ion-assisted deposition and milling were minimized by using electron beam deposition for the protective C and Pt “strap” layers. The combined results of STEM bright-field imaging and energy-dispersive x-ray (EDX) spectral imaging with a 2 nm probe size revealed a sequence of four microstructurally and compositionally distinct regions within the top 100 nm of the sample (Fig. 3). Compositional line-profiles across these regions were extracted and quantified from EDX spectrum images (Figs. 3,4). Moving inward from the surface, Region D is a porous, low-density, layer that is Fe-rich relative to stoichiometric ilmenite (Fe/Ti atomic ratio of ~ 3 -4). High-resolution TEM imaging and

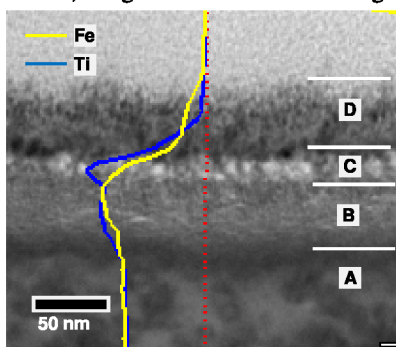


Figure 3. Bright-field STEM image of FIB-sectioned top surface of irradiated ilmenite grain, with compositional line profiles for Fe and Ti superposed.

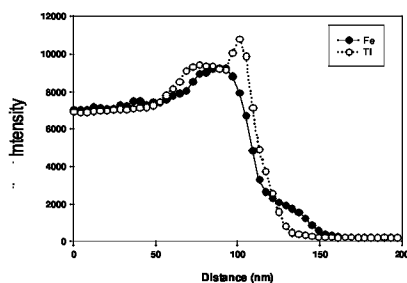


Figure 4. Background-subtracted EDX peak intensity profiles for Fe and Ti extracted from compositional spectrum image in Fig. 3.

EDX analysis indicate this layer is comprised predominantly of a network of nanophase Fe metal particles, although other phases may be present. At a depth of ~ 50 nm, Region D transitions to a 10-20 nm-thick Fe-depleted layer (Region C; Fe/Ti = 0.6-0.75). Although similarly porous like Region D, the void spaces in Region C are larger and appear to be He-“bubbles” formed by coalescence of implanted He in voids or vacancy clusters. Below Region C, the Fe/Ti atomic ratio shifts briefly to near unity before changing, in

Region B, to a second set of slightly Fe-depleted values (Fe/Ti ~ 0.8 -0.9). Region B is about 50 nm thick and transitions to the bottom or “base” layer of un-altered ilmenite at a depth of ~ 100 nm.

Discussion: Allowing for reasonable changes in target density during the irradiation, there is qualitative agreement between the ~ 100 nm total thickness of the altered surface layers and He⁺ ion range data from SRIM calculations [5]. This supports the interpretation that the observed effects are from radiation processing, but it is notable that the final He⁺ dose did not result in amorphization of the sample at any depth. If the He⁺ dose is converted to ion-deposited atomic collision energy (E_d) using SRIM, our results place a lower limit on the threshold E_d for ilmenite amorphization of 120 keV/nm³, roughly an order of magnitude higher than the E_d values for silicates [6]. The complex microstructural and composition changes in the sample may suggest, however, that amorphization is overshadowed, or possibly prevented, by conversion of the irradiated region to “non-ilmenite” bulk compositions/phase assemblages. For the top-most ~ 1 -5 nm surface region, the compositional changes are dominated by a dramatic loss of O relative to cations due to preferential sputtering. The associated metallization of Fe in this top-most region is shown by TEM to extend well below the typical ~ 1 -5 nm surface depth probed by XPS. Preferential sputter removal aided by radiation enhanced diffusion of O from this depth is not, however, inconsistent with other studies [7].

The Fe/Ti compositional relations observed by TEM show for the first time that ion radiation alone is capable of broadly re-producing the “surface Fe enriched /interior Fe depleted” compositional pattern on natural lunar ilmenites [1,3]. Details such as the “double-dip” in the Fe/Ti ratio and presence of He bubbles in the experimental sample remain to be matched with the natural ilmenite rims samples, but as noted in [3], the natural samples are subjected to a range of additional processes that may operate to smooth out or removed these features. Our finding that XPS shows Ti/Fe > 1 on the top-most surface of the “D” layer, when TEM suggests this layer is mostly Fe metal, likely reflects the details of a surface reconstruction layer that XPS measures but TEM does not.

References: [1] Christoffersen R. et al. (1996) *Met. & Planet. Sci.*, 31, 835-848. [2] Berantowicz, T.J. et al. (1994) *LPS XXV*, 105-106. [3] Zhang S. et al. (2010) *LPS XLI*, this volume. [4] Keller L.P. et al. (1997) *Geochim. Cosmo. Acta*, 61, 2331-2341. [5] Ziegler, J.F. et al. (2006) *Stopping and Range of Ions in Matter* <http://srim.org>. [6] Wang, L.M and Ewing, R. (1992) *MRS Bulletin*, 17, 38-44. [7] Cheng Y.-T. et al. (1991) *Mater. Res. Soc. Sym. Proc* 201, 75-86.